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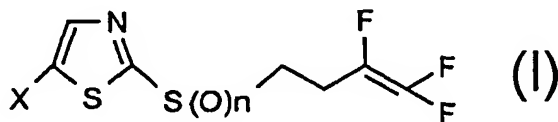
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(54) Title: **NEMATICIDAL TRIFLUOROBUTENES**



(57) Abstract: The invention relates to compounds of formula (I) in which X represents halogen, and n represents 0, 1 or 2, to a process for their preparation and to their use as nematicides.

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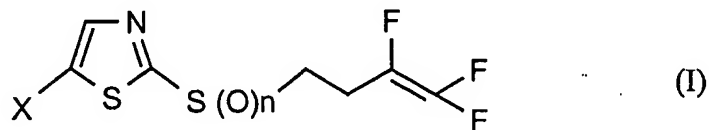
**WO 01/02378 A1**

## NEMATICIDAL TRIFLUOROBUTENES

The present invention relates to novel trifluorobutenes and their use as nematicides.

5 US Patent No. 3,518,172 describes trifluorobutenyl compounds which have nematicidal activity. Japanese Laid-open Patent Publication (PCT) No. 500037/1988 (= WO 86/07590) also describes that some kinds of polyhaloalkene compounds have nematicidal activity. Further, WO 95/24403 describes that 4,4-difluorobutenyl compounds have nematicidal activity. Japanese Laid-open Patent Application No.  
10 176141/1997 mentions thiazole derivatives having insecticidal and acaricidal activity.

There have now been found novel trifluorobutenes of the formula (I)



15

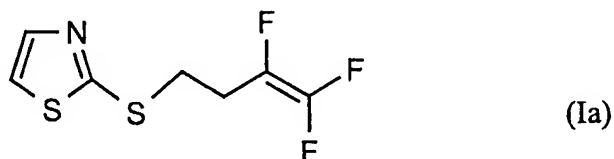
in which

X represents halogen and

20

n represents 0, 1 or 2.

The compounds of the formula (I) in which n represents 0 can be obtained when trifluorobutenes of the formula (Ia)



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- 2 -

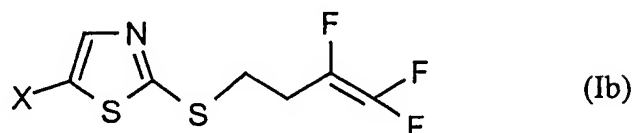
are reacted with a halogenating agent, optionally in the presence of one or more inert diluents (process (A)).

The compounds of the formula (I) in which

5

n represents 1 or 2

can be obtained when compounds of the formula (Ib)



10

in which

X is the same as defined above

15

are reacted with an oxidizing agent, optionally in the presence of one or more inert diluents (process (B)).

The compounds of the formula (I) of the present invention have strong nematocidal activity and show good compatibility with various crops. According to the present invention the compounds of the formula (I) have surprisingly strong nematocidal activity compared with the known compounds described in the aforementioned literature.

20

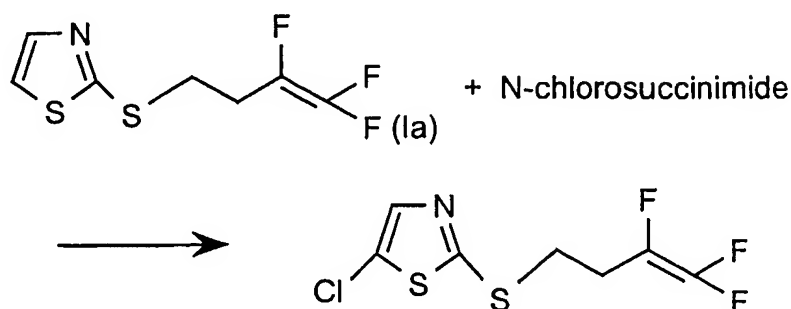
In the present specification X preferably represents fluoro, chloro or bromo. X particularly preferably represents fluoro or chloro. X very particularly preferably represents chloro.

25

In the present specification n preferably represents 0 or 2. n particularly preferably represents 2.

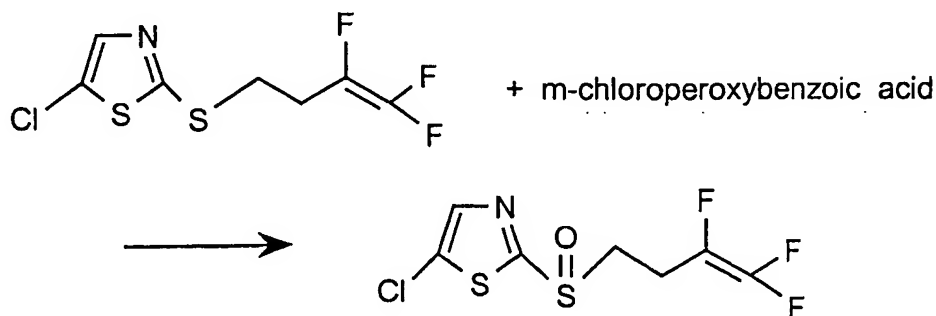
Process (A) for preparing compounds of the formula (I) of the present invention can be represented by the following reaction scheme in which N-chlorosuccinimide is exemplarily used as halogenating agent:

5



Process (B) for preparing compounds of the formula (I) of the present invention can be represented by the following reaction in which 5-chloro-2-(3,4,4-trifluoro-3-butenylthio)thiazole is used as a starting material and m-chloroperoxybenzoic acid is exemplarily used as oxidizing agent.

10



2-(3,4,4-trifluoro-3-butenylthio)-thiazole is a known compound described in Japanese Laid-open Patent Publication (PCT) No. 500037/1988 (= WO 86/07590). Compounds of formula (Ib), which are used as starting material in process (B), correspond to the compounds of the formula (I) of the present invention in which n represents 0 and can be synthesized according to the aforementioned process (A).

20

Halogenating agents used in Process (A) can be agents usually used for this purpose in organic chemistry and which are known to a person skilled in the art, including for example sulfonyl chloride, N-chlorosuccinimide, N-bromosuccinimide, trichloroisocyanuric acid, potassium fluoride, sodium chlorate, phosphorus pentachloride, titanium (IV) chloride, chlorine gas, bromine, iodine etc.

Oxidizing agents used for the oxidation of the above-mentioned compounds of the formula (Ib) in process (B) can be agents usually used for this purpose in organic chemistry and which are known to a person skilled in the art including for example hydrogen peroxide water, m-chloroperoxybenzoic acid, peroxyacetic acid, peroxybenzoic acid, magnesium monoperoxyphthalate, potassium peroxymonosulfate, etc.

The reaction of the above-mentioned process (A) is preferably conducted in the presence of an adequate diluent. Diluents which can be used in this process can for example be water; aliphatic, alicyclic and aromatic hydrocarbons (which can be optionally chlorinated) such as hexane, cyclohexane, petroleum ether, ligroine, benzene, methylene chloride, chloroform, carbon tetrachloride, ethylene chloride, chlorobenzene etc.; ethers, such as diethyl ether, methyl ethyl ether, di-isopropyl ether, dibutyl ether, propylene oxide, dioxane, tetrahydrofuran etc.; nitriles, such as acetonitrile, propionitrile, acrylonitrile etc.; acid amides, such as dimethylformamide, dimethylacetamide, N-methylpyrrolidone etc.; sulfones and sulfoxides, such as dimethyl sulfoxide, sulfolane etc.

The reaction temperatures of process (A) according to the invention can be varied over a relatively wide range. In general, temperatures in a range of between 0 and 200°C, preferably between 20 and 150°C are employed. The process (A) according to the invention is generally carried out under normal pressure. However, it is possible to carry out the process (A) under elevated pressure or under reduced pressure, in general between 0.1 bar and 10 bar.

To carry out the process (A) according to the invention, the starting materials are

generally employed in approximately equimolar amounts. However, it is also possible to use one of the components in a relatively large excess. Work-up is carried out according to customary methods (cf. the preparation examples).

5 For example, the compound of the formula (I) in which n represents 0 and X represents chloro can be obtained by reacting 1-1.2 moles of N-chlorosuccinimide with 1 mole of 2-(3,4,4-trifluoro-3-butenylthio)thiazole in carbon tetrachloride under reflux by heating.

10 The reaction of the above-mentioned process (B) is preferably conducted in the presence of an adequate diluent. Diluents which can be used in this process can for example be water; aliphatic, alicyclic and aromatic hydrocarbons (which can be optionally chlorinated), such as hexane, cyclohexane, petroleum, ether, ligroine, benzene, toluene, xylene, methylene chloride, chloroform, carbon tetrachloride,  
15 ethylene chloride, chlorobenzene etc.; ethers, such as diethyl ether, methyl ethyl ether, di-isopropyl ether, dibutyl ether, propylene oxide, dioxane, tetrahydrofuran etc.; nitriles, such as acetonitrile, propionitrile, acrylonitrile etc.; alcohols, for example methanol, ethanol, isopropanol, butanol, ethylene glycol etc.; esters, for example ethyl acetate, amyl acetate etc.; acid amides, for example dimethyl-  
20 formamide, dimethylacetamide, N-methylpyrrolidone etc.; sulfones and sulfoxides, for example dimethyl sulfoxide, sulfolane etc.; carboxylic acids, for example formic acid, acetic acid etc.

The reaction temperatures of process (B) according to the invention can be varied  
25 over a relatively wide range: In general, temperatures in a range of between 0 and 150°C, preferably between 0 and 120°C are employed. The process (B) according to the invention is generally carried out under normal pressure. However, it is also possible to carry out the process (B) under elevated pressure or under reduced pressure, in general between 0.1 bar and 10 bar.

30 To carry out the process (B) according to the invention, the starting materials are generally employed in approximately equimolar amounts. However, it is also

possible to use one of the components in a relatively large excess. Work-up is carried out according to customary methods (cf. the preparation examples).

5 For example, compounds of the formula (I) in which n represents 1 can be obtained by reacting, 1-2 moles of m-chloroperoxybenzoic acid with 1 mole of the compound of the formula (Ib) in methylene chloride under cooling with ice.

10 The compounds of the formula (I) according to the present invention show strong controlling activity against nematodes. They can, therefore, be efficiently used as nematicidal agents. The compounds of the formula (I) of the present invention do not exhibit phytotoxicity against crops and can be used for controlling harmful nematodes.

15 The compounds according to the invention can be used, for example, against nematodes such as *Pratylenchus* spp., *Globodera* spp., such as *Globodera rostochiensis* wollenweber, *Heterodera* spp., such as *Heterodera glycines* ichinohe, *Meloidogyne* spp., *Aphelenchoides* spp., such as *Aphelenchoides basseyi* christie, *Radopholus similis*, *Ditylenchus dipsaci*, *Tylenchulus semipenetrans*, *Longidorus* spp., *Xiphinema* spp., *Trichodorus* spp., *Bursaphelenchus* spp., such as  
20 *Bursaphelenchus xylophilis* etc.

The compounds according to the invention are especially useful for combating *Pratylenchus* spp., *Globodera rostochiensis* wollenweber, *Heterodera glycines* ichinohe, *Meloidogyne* spp., *Aphelenchoides basseyi* christie, *Bursaphelenchus*  
25 *xylophilis*.

However, the use of the active compounds according to the invention is in no way restricted to these genera, but also extends in the same manner to other nematodes.

30 The active compounds can be converted into the customary formulations, such as solutions, emulsions, wettable powders, water dispersible granules, suspensions,

powders, dusting agents, foaming agents, pastes, soluble powders, granules, suspo-emulsion concentrates, microcapsules, fumigants, natural and synthetic materials impregnated with active compound and very fine capsules and polymeric substances.

5        These formulations are prepared in a known manner, for example by mixing the active compounds with extenders, that is liquid solvents, liquefied gas and/or solid diluents or carriers, if appropriate with the use of surface-active agents, that is emulsifiers and/or dispersants and/or foam-formers.

10       If the extender used is water, it is also possible to use, for example, organic solvents as auxiliary solvents. Suitable liquid solvents are essentially: aromatics, such as xylene, toluene, or alkylnaphthalenes, chlorinated aromatics and chlorinated aliphatic hydrocarbons, such as chlorobenzene, chloroethylenes or methylene chloride, aliphatic hydrocarbons, such as cyclohexane or paraffins, for example mineral oil  
15       fractions, mineral or vegetable oil, alcohols, such as butanol or glycol, and also their ethers and esters, ketones, such as acetone, methyl ethyl ketone, methyl isobutyl ketone or cyclohexanone, strongly polar solvents, such as dimethylformamide and dimethyl sulphoxide, and also water.

20       Liquefied gas diluents or carriers are liquefied substances which are gases at normal temperature and pressure. Liquefied gas diluents can be, for example, aerosol propellants such as butane, propane, nitrogen gas, carbon dioxide, halogenated hydrocarbons, etc.

25       Suitable solid carriers are:  
for example ammonium salts and ground natural minerals, such as kaolins, clays, talc, chalk, quartz, attapulgite, montmorillonite or diatomaceous earth, and ground synthetic minerals, such as finely divided silica, alumina and silicates; suitable solid carriers for granules are: for example crushed and fractionated natural rocks such as  
30       calcite, marble, pumice, sepiolite and dolomite, as well as synthetic granules of inorganic and organic meals, and granules of organic material such as sawdust,



coconut shells, maize cobs and tobacco stalks; suitable emulsifiers and/or foam-formers are: for example nonionic and anionic emulsifiers, such as polyoxyethylene fatty acid esters, polyoxyethylene fatty alcohol ethers, for example alkylaryl polyglycol ethers, alkylsulphonates, alkyl sulphates, arylsulphonates and protein hydrolysates; suitable dispersants are: for example lignin-sulphite waste liquors and methylcellulose.

Tackifiers such as carboxymethylcellulose and natural and synthetic polymers in the form of powders, granules or latices, such as gum arabic, polyvinyl alcohol and polyvinyl acetate, as well as natural phospholipids, such as cephalins and lecithins, and synthetic phospholipids, can be used in the formulations. Other additives can be mineral and vegetable oils.

It is possible to use colorants such as inorganic pigments, for example iron oxide, titanium oxide and Prussian Blue, and organic dyestuffs, such as alizarin dyestuffs, azo dyestuffs and metal phthalocyanine dyestuffs, and trace nutrients such as salts of iron, manganese, boron, copper, cobalt, molybdenum and zinc.

The formulations in general contain between 0.01 and 95 per cent by weight of active compound, preferably between 0.1 and 90%, particularly preferably between 0.5 and 90%.

The active compounds according to the invention, as such or in their formulations, can also be used in a mixture with known fungicides, bactericides, acaricides, nematocides or insecticides, to widen, for example, the activity spectrum or to prevent the development of resistance. In many cases, this results in synergistic effects, i.e. the activity of the mixture exceeds the activity of the individual components.

Examples of particularly advantageous mixing components are the following:

## Fungicides:

aldimorph, ampropylfos, ampropylfos potassium, andoprim, anilazine, azaconazole, azoxystrobin,

benalaxyl, benodanil, benomyl, benzamacril, benzamacril-isobutyl, bialaphos,  
5 binapacryl, biphenyl, bitertanol, blasticidin-S, bromuconazole, bupirimate, buthiobate,

calcium polysulphide, capsimycin, captafol, captan, carbendazim, carboxin, carvon, quinomethionate, chlobenthiazone, chlorfenazole, chloroneb, chloropicrin, chlorothalonil, chlozolate, clozylacon, cufraneb, cymoxanil, cyproconazole,  
10 cyprodinil, cyprofuram,

debacarb, dichlorophen, diclobutrazole, diclofluanid, diclomezine, dicloran, diethofencarb, difenoconazole, dimethirimol, dimethomorph, diniconazole, diniconazole-M, dinocap, diphenylamine, dipyrithione, ditalimfos, dithianon, dodemorph, dodine, drazoxolon,

15 ediphenphos, epoxiconazole, etaconazole, ethirimol, etridiazole,

famoxadon, fenapanil, fenarimol, fenbuconazole, fenfuram, fenitropan, fencpiclonil, fenpropidin, fenpropimorph, fentin acetate, fentin hydroxide, ferbam, ferimzone, fluazinam, flumetover, fluoromide, fluquinconazole, flurprimidol, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetyl-aluminium, fosetyl-sodium,  
20 fthalide, fuberidazole, furalaxyl, furametpyr, furcarbonil, furconazole, furconazole-cis, furmecyclox,

guazatine,

hexachlorobenzene, hexaconazole, hymexazole,

imazalil, imibenconazole, iminoctadine, iminoctadine albesilate, iminoctadine triacetate, iodocarb, ipconazole, iprobenfos (IBP), iprodione, irumamycin,  
25 isoprothiolane, isovaledione,

kasugamycin, kresoxim-methyl, copper preparations, such as: copper hydroxide, copper naphthenate, copper oxychloride, copper sulphate, copper oxide, oxine-copper and Bordeaux mixture,

mancopper, mancozeb, maneb, meferimzone, mepanipyrim, mepronil, metalaxyl,  
 metconazole, methasulfocarb, methfuroxam, metiram, metomeclam, metsulfovax,  
 mildiomyacin, myclobutanil, myclozolin,  
 nickel dimethyldithiocarbamate, nitrothal-isopropyl, nuarimol,  
 5 ofurace, oxadixyl, oxamocarb, oxolinic acid, oxycarboxim, oxyfenthiin,  
 paclobutrazole, pefurazoate, penconazole, pencycuron, phosdiphen, pimaricin,  
 piperalin, polyoxin, polyoxorim, probenazole, prochloraz, procymidone,  
 propamocarb, propanosine-sodium, propiconazole, propineb, pyrazophos, pyrifenoxy,  
 pyrimethanil, pyroquilon, pyroxyfur,  
 10 quinconazole, quintozone (PCNB),  
 sulphur and sulphur preparations,  
 tebuconazole, tecloftalam, tecnazene, tetracyclis, tetraconazole, thiabendazole,  
 thicyofen, thifluzamide, thiophanate-methyl, thiram, tioxyimid, tolclofos-methyl,  
 tolylfluanid, triadimefon, triadimenol, triazbutyl, triazoxide, trichlamide, tricyclazole,  
 15 tridemorph, triflumizole, triforine, triticonazole,  
 uniconazole,  
 validamycin A, vinclozolin, viniconazole,  
 zarilamide, zineb, ziram and also  
 Dagger G,  
 20 OK-8705,  
 OK-8801,  
 $\alpha$ -(1,1-dimethylethyl)- $\exists$ -(2-phenoxyethyl)-1H-1,2,4-triazole-1-ethanol,  
 $\alpha$ -(2,4-dichlorophenyl)- $\exists$ -fluoro-b-propyl-1H-1,2,4-triazole-1-ethanol,  
 $\alpha$ -(2,4-dichlorophenyl)- $\exists$ -methoxy-a-methyl-1H-1,2,4-triazole-1-ethanol,  
 25  $\alpha$ -(5-methyl-1,3-dioxan-5-yl)- $\exists$ -[[4-(trifluoromethyl)-phenyl]-methylene]-1H-1,2,4-  
 triazole-1-ethanol,  
 (5RS,6RS)-6-hydroxy-2,2,7,7-tetramethyl-5-(1H-1,2,4-triazol-1-yl)-3-octanone,  
 (E)-a-(methoxyimino)-N-methyl-2-phenoxy-phenylacetamide,  
 isopropyl 1-{2-methyl-1-[[[1-(4-methylphenyl)-ethyl]-amino]-carbonyl]-propyl}-carbamate,  
 30 1-(2,4-dichlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-ethanone O-(phenylmethyl) oxime,  
 1-(2-methyl-1-naphthalenyl)-1H-pyrrol-2,5-dione,

- 1-(3,5-dichlorophenyl)-3-(2-propenyl)-2,5-pyrrolidinedione,  
1-[(diiodomethyl)-sulphonyl]-4-methyl-benzene,  
1-[[2-(2,4-dichlorophenyl)-1,3-dioxolan-2-yl]-methyl]-1H-imidazole,  
1-[[2-(4-chlorophenyl)-3-phenyloxiranyl]-methyl]-1H-1,2,4-triazole,  
5 1-[1-[2-[(2,4-dichlorophenyl)-methoxy]-phenyl]-ethenyl]-1H-imidazole,  
1-methyl-5-nonyl-2-(phenylmethyl)-3-pyrrolidinole,  
2',6'-dibromo-2-methyl-4'-trifluoromethoxy-4'-trifluoro-methyl-1,3-thiazole-5-  
carboxanilide,  
2,2-dichloro-N-[1-(4-chlorophenyl)-ethyl]-1-ethyl-3-methyl-cyclopropane-  
10 carboxamide,  
2,6-dichloro-5-(methylthio)-4-pyrimidinyl thiocyanate,  
2,6-dichloro-N-(4-trifluoromethylbenzyl)-benzamide,  
2,6-dichloro-N-[[4-(trifluoromethyl)-phenyl]-methyl]-benzamide,  
2-(2,3,3-triiodo-2-propenyl)-2H-tetrazole,  
15 2-[(1-methylethyl)-sulphonyl]-5-(trichloromethyl)-1,3,4-thiadiazole,  
2-[[6-deoxy-4-O-(4-O-methyl- $\beta$ -D-glycopyranosyl)- $\alpha$ -D-glucopyranosyl]-amino]-4-  
methoxy-1H-pyrrolo[2,3-d]pyrimidine-5-carbonitrile,  
2-aminobutane,  
2-bromo-2-(bromomethyl)-pentanedinitrile,  
20 2-chloro-N-(2,3-dihydro-1,1,3-trimethyl-1H-inden-4-yl)-3-pyridinecarboxamide,  
2-chloro-N-(2,6-dimethylphenyl)-N-(isothiocyanatomethyl)-acetamide,  
2-phenylphenol (OPP),  
3,4-dichloro-1-[4-(difluoromethoxy)-phenyl]-1H-pyrrol-2,5-dione,  
3,5-dichloro-N-[cyano-[(1-methyl-2-propynyl)-oxy]-methyl]-benzamide,  
25 3-(1,1-dimethylpropyl-1-oxo-1H-indene-2-carbonitrile),  
3-[2-(4-chlorophenyl)-5-ethoxy-3-isoxazolidinyl]-pyridine,  
4-chloro-2-cyano-N,N-dimethyl-5-(4-methylphenyl)-1H-imidazole-1-sulphonamide,  
4-methyl-tetrazolo[1,5-a]quinazolin-5(4H)-one,  
8-(1,1-dimethylethyl)-N-ethyl-N-propyl-1,4-dioxaspiro[4.5]decane-2-methanamine,  
30 8-hydroxyquinoline sulphate,  
9H-xanthene-2-[(phenylamino)-carbonyl]-9-carboxylic hydrazide,

- bis-(1-methylethyl) 3-methyl-4-[(3-methylbenzoyl)-oxy]-2,5-thiophenedicarboxylate,  
 cis-1-(4-chlorophenyl)-2-(1H-1,2,4-triazol-1-yl)-cycloheptanol,  
 cis-4-[3-[4-(1,1-dimethylpropyl)-phenyl-2-methylpropyl]-2,6-dimethyl-morpholine  
 hydrochloride,
- 5 ethyl [(4-chlorophenyl)-azo]-cyanoacetate,  
 potassium hydrogen carbonate,  
 methanetetrahiol sodium salt,  
 methyl 1-(2,3-dihydro-2,2-dimethyl-1H-inden-1-yl)-1H-imidazole-5-carboxylate,  
 methyl N-(2,6-dimethylphenyl)-N-(5-isoxazolylcarbonyl)-DL-alaninate,
- 10 methyl N-(chloroacetyl)-N-(2,6-dimethylphenyl)-DL-alaninate,  
 N-(2,3-dichloro-4-hydroxyphenyl)-1-methyl-cyclohexanecarboxamide,  
 N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-furanyl)-acetamide,  
 N-(2,6-dimethylphenyl)-2-methoxy-N-(tetrahydro-2-oxo-3-thienyl)-acetamide,  
 N-(2-chloro-4-nitrophenyl)-4-methyl-3-nitro-benzenesulphonamide,
- 15 N-(4-cyclohexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidineamine,  
 N-(4-hexylphenyl)-1,4,5,6-tetrahydro-2-pyrimidineamine,  
 N-(5-chloro-2-methylphenyl)-2-methoxy-N-(2-oxo-3-oxazolidinyl)-acetamide,  
 N-(6-methoxy)-3-pyridinyl)-cyclopropanecarboxamide,  
 N-[2,2,2-trichloro-1-[(chloroacetyl)-amino]-ethyl]-benzamide,
- 20 N-[3-chloro-4,5-bis(2-propinyloxy)-phenyl]-N'-methoxy-methanimidamide,  
 N-formyl-N-hydroxy-DL-alanine-sodium salt,  
 O,O-diethyl [2-(dipropylamino)-2-oxoethyl]-ethylphosphoramidothioate,  
 O-methyl S-phenyl phenylpropylphosphoramidothioate,  
 S-methyl 1,2,3-benzothiadiazole-7-carbothioate, and
- 25 spiro[2H]-1-benzopyran-2,1'(3'H)-isobenzofuran]-3'-one,

#### Bactericides:

- bronopol, dichlorophen, nitrapyrin, nickel dimethyldithiocarbamate, kasugamycin,  
 octhilinone, furancarboxylic acid, oxytetracyclin, probenazole, streptomycin,
- 30 tecloftalam, copper sulphate and other copper preparations.

## Insecticides / acaricide / nematicides:

abamectin, acephate, acetamiprid, acrinathrin, alanycarb, aldicarb, aldoxycarb, alpha-cypermethrin, alphamethrin, amitraz, avermectin, AZ 60541, azadirachtin, azamethiphos, azinphos A, azinphos M, azocyclotin,

- 5 Bacillus popilliae, Bacillus sphaericus, Bacillus subtilis, Bacillus thuringiensis, baculoviruses, Beauveria bassiana, Beauveria tenella, bendiocarb, benfuracarb, bensultap, benzoximate, betacyfluthrin, bifenazate, bifenthrin, bioethanomethrin, biopermethrin, BPMC, bromophos A, bufencarb, buprofezin, butathiofos, butocarboxim, butylpyridaben,
- 10 cadusafos, carbaryl, carbofuran, carbophenothion, carbosulfan, cartap, chloethocarb, chlorethoxyfos, chlorfenapyr, chlorfenvinphos, chlorfluazuron, chlormephos, chlorpyrifos, chlorpyrifos M, chlovaporthrin, cis-resmethrin, cispermethrin, clocythrins, cloethocarb, clofentezine, cyanophos, cycloprene, cycloprothrin, cyfluthrin, cyhalothrin, cyhexatin, cypermethrin, cyromazine,
- 15 deltamethrin, demeton M, demeton S, demeton-S-methyl, diafenthiuron, diazinon, dichlorvos, diflubenzuron, dimethoat, dimethylvinphos, diofenolan, disulfoton, docusat-sodium, dofenapyn,  
e-flusilanate, emamectin, empenethrin, endosulfan, Entomophthora spp., esfenvalerate, ethiofencarb, ethion, ethoprophos, etofenprox, etoxazole, etrimfos,
- 20 fenamiphos, fenazaquin, fenbutatin oxide, fenitrothion, fenothiocarb, fenoxacrim, fenoxycarb, fenpropathrin, fenpyrad, fenpyrithrin, fenpyroximate, fenvalerate, fipronil, fluazinam, fluazuron, flubrocycythrinate, flucycloxuron, flucythrinate, flufenoxuron, flutenzine, fluvalinate, fonophos, fosmethilan, fosthiazate, fubfenprox, furathiocarb,
- 25 granulosus viruses,  
halofenozide, HCH, heptenophos, hexaflumuron, hexythiazox, hydroprene, imidacloprid, isazofos, isofenphos, isoxathion, ivermectin,  
nuclear polyhedrosis viruses,  
lambda-cyhalothrin, lufenuron

malathion, mecarbam, metaldehyde, methamidophos, Metharhizium anisopliae, Metharhizium flavoviride, methidathion, methiocarb, methomyl, methoxyfenozide, metolcarb, metoxadiazone, mevinphos, milbemectin, monocrotophos, naled, nitenpyram, nithiazine, novaluron,

5 omethoat, oxamyl, oxydemethon M, Paecilomyces fumosoroseus, parathion A, parathion M, permethrin, phenthoat, phorat, phosalone, phosmet, phosphamidon, phoxim, pirimicarb, pirimiphos A, pirimiphos M, profenofos, promecarb, propoxur, prothiofos, prothoat, pymetrozine, pyraclofos, pyresmethrin, pyrethrum, pyridaben, pyridathion, pyrimidifen,

10 pyriproxyfen, quinalphos, ribavirin, salithion, sebufos, silafluofen, spinosad, sulfotep, sulprofos, tau-fluvalinate, tebufenozide, tebufenpyrad, tebupirimiphos, teflubenzuron,

15 tefluthrin, temephos, temivinphos, terbufos, tetrachlorvinphos, theta-cypermethrin, thiamethoxam, thiapronil, thiatriphos, thiocyclam hydrogen oxalate, thiodicarb, thiofanox, thuringiensin, traloccythrin, tralomethrin, triarathene, triazamate, triazophos, triazuron, trichlophenidine, trichlorfon, triflumuron, trimethacarb, vamidothion, vaniliprole, Verticillium lecanii,

20 YI 5302, zeta-cypermethrin, zolaprofos, (1R-cis)-[5-(phenylmethyl)-3-furanyl]-methyl 3-[(dihydro-2-oxo-3(2H)-furanylidene)-methyl]-2,2-dimethylcyclopropanecarboxylate, (3-phenoxyphenyl)-methyl 2,2,3,3-tetramethylcyclopropanecarboxylate,

25 1-[(2-chloro-5-thiazolyl)methyl]tetrahydro-3,5-dimethyl-N-nitro-1,3,5-triazine-2(1H)-imine, 2-(2-chloro-6-fluorophenyl)-4-[4-(1,1-dimethylethyl)phenyl]-4,5-dihydro-oxazole, 2-(acetyloxy)-3-dodecyl-1,4-naphthalenedione, 2-chloro-N-[[[4-(1-phenylethoxy)-phenyl]-amino]-carbonyl]-benzamide,

30 2-chloro-N-[[[4-(2,2-dichloro-1,1-difluoroethoxy)-phenyl]-amino]-carbonyl]-benzamide,

3-methylphenyl propylcarbamate.

4-[4-(4-ethoxyphenyl)-4-methylpentyl]-1-fluoro-2-phenoxy-benzene,  
4-chloro-2-(1,1-dimethylethyl)-5-[[2-(2,6-dimethyl-4-phenoxyphenoxy)ethyl]thio]-  
3(2H)-pyridazinone,

5 4-chloro-2-(2-chloro-2-methylpropyl)-5-[(6-iodo-3-pyridinyl)methoxy]-3(2H)-  
pyridazinone,

4-chloro-5-[(6-chloro-3-pyridinyl)methoxy]-2-(3,4-dichlorophenyl)-3(2H)-  
pyridazinone,

Bacillus thuringiensis strain EG-2348,

10 [2-benzoyl-1-(1,1-dimethylethyl)-hydrazinobenzoic acid,  
2,2-dimethyl-3-(2,4-dichlorophenyl)-2-oxo-1-oxaspiro[4.5]dec-3-en-4-yl butanoate,  
[3-[(6-chloro-3-pyridinyl)methyl]-2-thiazolidinylidene]-cyanamide,  
dihydro-2-(nitromethylene)-2H-1,3-thiazine-3(4H)-carboxaldehyde,  
ethyl [2-[[1,6-dihydro-6-oxo-1-(phenylmethyl)-4-pyridazinyl]oxy]ethyl]-carbamate,

15 N-(3,4,4-trifluoro-1-oxo-3-butenyl)-glycine,  
N-(4-chlorophenyl)-3-[4-(difluoromethoxy)phenyl]-4,5-dihydro-4-phenyl-1H-  
pyrazole-1-carboxamide,

N-[(2-chloro-5-thiazolyl)methyl]-N'-methyl-N''-nitro-guanidine,

N-methyl-N'-(1-methyl-2-propenyl)-1,2-hydrazinedicarbothioamide,

20 N-methyl-N'-2-propenyl-1,2-hydrazinedicarbothioamide,

O,O-diethyl [2-(dipropylamino)-2-oxoethyl]-ethylphosphoroamidothioate.

A mixture with other known active compounds, such as herbicides, or with fertilizers  
and growth regulators is also possible.

25

Furthermore, when used as nematicides, the active compounds according to the  
invention can be present in their commercial formulations and in the use forms,  
prepared from these formulations, as a mixture with synergists. Synergists are  
compounds which increase the action of the active compounds, without it being  
30 necessary for the synergist added to be active itself.



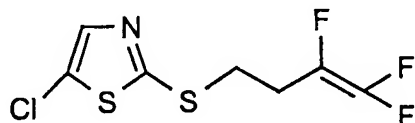
The active-compound content of the use forms prepared from the commercial formulations can vary within wide limits. The active-compound concentration of the use forms can be from 0.0000001 to 95% by weight of active compound, preferably between 0.0001 and 1% by weight.

5 Application is carried out in a customary manner adapted to the use forms.

The preparation and the use of the compounds according to the present invention will be described more specifically by the following examples. However, the present invention should not be restricted to them in any way. "Parts" mean "parts by  
10 weight" unless specified otherwise.

### Preparation Examples

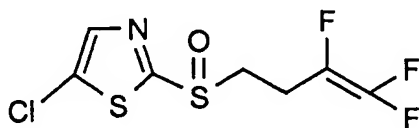
#### 15 Example 1



2-(3,4,4-Trifluoro-3-butenylthio)thiazole (6.75 g, 30 mM) is dissolved in carbon  
20 tetrachloride (60 ml). N-chlorosuccinimide (4.8 g) is added to the solution and  
refluxed for 18 hours by heating. As soon as the reaction has reached room  
temperature, the mixture is filtered and the solvent is distilled off. The concentrate is  
purified by column chromatography (eluent: hexane/ethyl acetate = 90/10) to obtain  
5-chloro-2-(3,4,4-trifluoro-3-butenylthio)thiazole as pale yellow liquid ( $n_D^{20}$  1.5326).

25

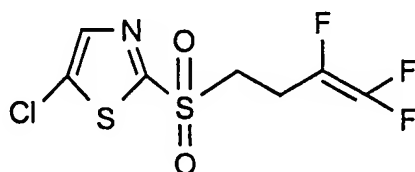
#### Example 2



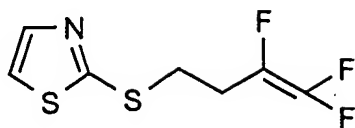
5-Chloro-2-(3,4,4-trifluoro-3-butenylthio)thiazole (2.07 g, 8 mM) is dissolved in chloroform (40 ml). m-chloroperoxybenzoic acid (1.38 g) is added to the solution under ice cooling (temperature below 4°C) and further stirred for 8 hours at a temperature below 4°C.

10% sodium thiosulfate is added to the solution and the solution is then fractionated. The chloroform layer is washed with 5% aqueous solution of sodium hydroxide and dried over unhydrous magnesium sulfate. The solvent is distilled off and the concentrate is purified by column chromatography (eluent: hexane/ethyl acetate = 90/10) to obtain 5-chloro-2-(3,4,4-trifluoro-3-butenylsulfinyl)thiazole (1.5 g) as pale yellow liquid ( $n_D^{20}$  1.5380).

### Example 3



To the solution of 5-chloro-2-(3,4,4-trifluoro-3-butenylthio)thiazole (2.60 g, 10 mM) and acetic acid (28 g) 31% hydrogen peroxide water (3.29 g) is added and stirred at 55-60°C for 6 hours. After cooling to 5°C the reaction mixture is adjusted to pH 6 by adding an appropriate amount of an aqueous solution of sodium hydroxide, diluted with water and extracted three times with chloroform (25 ml). The chloroform layer is washed with water, 10% sodium thiosulfate and water in this order, and dried over unhydrous sodium sulfate. The solvent is distilled off and the concentrate is purified by column chromatography (eluent: hexane/ethyl acetate = 90/10) to obtain 5-chloro-2-(3,4,4-trifluoro-3-butenylsulfonyl)thiazole (2.2 g) as pale yellow liquid ( $n_D^{20}$  1.5205).

**Reference Example**

5      2-Mercaptothiazole (5.18 g), potassium carbonate (6.72 g) and 4-bromo-1,1,2-trifluorobutene-1 (9.21 g) are refluxed in acetonitrile (60 ml) in the presence of argon gas for 6 hours by heating. After the reaction mixture has reached room temperature, it is filtered and the solvent is distilled off. The residue is dissolved in dichloromethane and washed with 5% aqueous solution of sodium hydroxide and  
10      water in this order. It is dried over anhydrous sodium sulfate and purified by column chromatography (eluent: dichloromethane) to obtain 2-(3,4,4-trifluoro-3-butenylthio)thiazole (8.6 g) as pale yellow liquid ( $n_D^{20}$  1.5200).

**Use Examples**

15

**Example 1**      Test against *Meloidogyne* spp. (Soil pot test)

Preparation of test agent:

1 Part of the active compound is impregnated to 99 parts of pumice to obtain fine  
20      granules.

Test method:

The test agent prepared as mentioned above was added to soil contaminated with *Meloidogyne incognita* to a chemical concentration of 10 ppm and homogeneously  
25      mixed by stirring. A pot (1/5000 are) was filled with the soil. About 20 seeds of tomato (variety: Kurihara) were sown per pot. After cultivation in a greenhouse for 4 weeks, they were carefully pulled out not to damage the roots and the root knot index and the controlling effect were determined as follows.

- Degree of damage
- 0: No knots were formed (Complete control).
  - 1: A few knots were formed.
  - 2: Knots were formed to a medium extent.
  - 3: Knots were formed to an intense extent.
  - 4: Knots were formed to the most intense extent (which corresponds to non-treatment).

5

10

$$\text{Root knot index} = \frac{\sum (\text{degree of damage} \times \text{number of individuals})}{\text{Total number of tested individuals} \times 4} \times 100$$

The controlling effect of the compounds tested can then be evaluated according to the following equation:

15

$$\text{Controlling effect [\%]} = \frac{(\text{Root knot index at non-treated area} - \text{Root knot index at treated area})}{\text{Root knot index at non-treated area}} \times 100$$

20

The evaluation of the controlling effects of the compounds according to the present invention was done on the basis of the values of the controlling effect which can be obtained in the above-mentioned way and were connected with the following standards:

25

- a: Controlling effect 100-71%
- b: Controlling effect 70-50%
- c: Controlling effect less than 50%
- d: Controlling effect 0%

30

Results are shown in the following Table 1.

Table 1

Compound Ex. No.	Concentration of active ingredient [ppm]	Evaluation of controlling effect
1	10	a
2	10	a
3	10	a

**Formulation Examples**

5

**Example 1** (Granule)

10 To a mixture of 10 parts of a compound according to the present invention (Example No. 1), 30 parts of bentonite (montmorillonite), 58 parts of talc and 2 parts of ligninsulphonate salt, 25 parts water are added, well kneaded, worked up into granules of 10-40 mesh with the help of an extrusion granulator and dried at 40-50°C to obtain granules.

**Example 2** (Granule)

15

95 Parts of clay mineral particles having a particle diameter distribution of 0.2-2 mm are put into a rotary mixer. While rotating it, 5 parts of a compound according to the present invention (Example No. 2) are sprayed onto the mineral particles together with a liquid diluent to obtain uniformly wetted particles and the particles are then  
20 dried at 40-50°C to obtain granules.

**Example 3** (Emulsifiable concentrates)

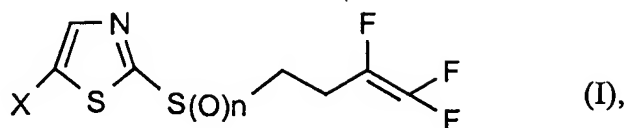
25 30 Parts of a compound according to the present invention (Example No. 3), 55 parts of xylene, 8 parts of polyoxyethylene alkyl phenyl ether and 7 parts of calcium alkylbenzenesulphonate are mixed and stirred to obtain an emulsion.

Example 4 (Wettable powder)

5 15 parts of a compound according to the present invention (Example No. 1), 80 parts of a mixture of white carbon (hydrous amorphous silicon oxide fine powders) and powder clay (1:5), 2 parts of sodium alkylbenzenesulphonate and 3 parts of sodium alkylnaphthalenesulphonate-formalin-condensate are crushed and mixed together to obtain a wettable powder.

Claims

1. Compounds of the formula (I)



wherein

X represents halogen, and

10 n represents 0, 1 or 2.

2. Compounds of the formula (I) according to claim 1, wherein

X represents fluoro, chloro or bromo, and

15

n represents 0 or 2.

3. Compounds of the formula (I) according to claim 1 or claim 2, wherein

20 X represents chloro or bromo, and

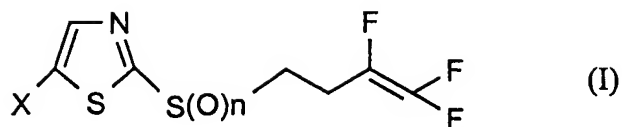
n represents 2.

4. Compounds of the formula (I) according to claims 1 to 3, wherein

25

X represents chloro.

5. Process for preparing compounds of the formula (I)



wherein

X is as defined in claims 1 to 4, and

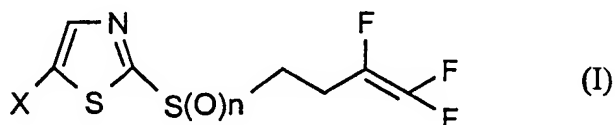
5

n represents 0,

characterized in that 2-(3,4,4-trifluoro-3-butenylthio)thiazole is reacted with a halogenating agent, if appropriate in the presence of inert solvents.

10

6. Process for preparing compounds of the formula (I)



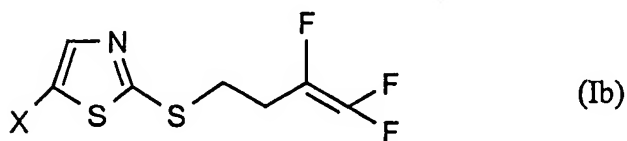
wherein

15

n represents 1 or 2, and

X is as defined in claims 1 to 4, characterized in that compounds of the formula (Ib)

20



wherein

X is as defined in claims 1 to 4.

25

are reacted with an oxidizing agent, if appropriate in the presence of inert



solvents.

7. Nematicidal compositions, characterized in that they contain at least one compound of the formula (I) according to claims 1 to 4.
- 5 8. A method of combating nematodes, characterized in that compounds of the formula (I) according to claims 1 to 4 are allowed to act on nematodes and/or their habitat.
- 10 9. Use of the compounds of the formula (I) according to claims 1 to 4 for combating nematodes.
10. Process for preparing nematicidal compositions, characterized in that the compounds of the formula (I) according to claims 1 to 4 are mixed with  
15 extenders and/or surface active agents.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/IB 00/00868

**A. CLASSIFICATION OF SUBJECT MATTER**  
 IPC 7 C07D277/36 A01N43/78

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C07D A01N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the International search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, CHEM ABS Data

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	WO 86 07590 A (FMC CORPORATION) 31 December 1986 (1986-12-31) cited in the application the whole document, particularly example 16	1-10
Y	WO 95 24403 A (ZENECA LIMITED) 14 September 1995 (1995-09-14) cited in the application the whole document, particularly pages 15-19, table VII, and examples VII.1-VII.16	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

19 September 2000

Date of mailing of the international search report

29/09/2000

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Allard, M

## INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/IB 00/00868

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 8607590 A	31-12-1986	AU 601656 B	13-09-1990
		AU 6122986 A	13-01-1987
		BR 8606746 A	13-10-1987
		CA 1277668 A	11-12-1990
		CN 86104207 A	01-04-1987
		DK 84387 A	19-02-1987
		EP 0228447 A	15-07-1987
		HU 42424 A	28-07-1987
		HU 204022 B	28-11-1991
		OA 8484 A	29-07-1988
		ZA 8604637 A	24-02-1988
		JP 63500037 T	07-01-1988
		MX 9249 A	01-12-1993
		US 4952580 A	28-08-1990
WO 9524403 A	14-09-1995	AP 649 A	29-05-1998
		AU 685242 B	15-01-1998
		AU 1816495 A	25-09-1995
		BG 100900 A	31-07-1997
		BR 9507042 A	09-09-1997
		CA 2182520 A	14-09-1995
		CN 1143958 A	26-02-1997
		CZ 9602632 A	11-12-1996
		EG 20790 A	29-03-2000
		EP 0749433 A	27-12-1996
		FI 963539 A	09-09-1996
		HU 74902 A,B	28-02-1997
		JP 9510197 T	14-10-1997
		LV 11686 A,B	20-02-1997
		NO 963776 A	07-11-1996
		NZ 281267 A	24-11-1997
		PL 316175 A	23-12-1996
		SK 114896 A	09-04-1997
		US 5705516 A	06-01-1998
		US 5912243 A	15-06-1999

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